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WASTES INTO PRODUCTION

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CERAMIC MATERIALS FROM LOW-MELTING CLAYS MODIFIED BY INDUSTRIAL WASTES FROM A GLASS-FIBER PLANT

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The wastes from the production of glass fiber can be used not only to solve a serious ecological problem but also to increase the quality of construction ceramic articles produced at brick manufacturing plants.

Key words: glass-fiber wastes, fusible clays, construction ceramic.

Petroleum-chemistry enterprises are undergoing rapid growth. However, the volumes of industrial wastes, whose collection and disposal are becoming serious economic and environmental problems, are growing at the same time. It is indicated in [1] that more than 2000 ha is allotted yearly for holding solid wastes from industrial enterprises. At the same time the consumption of resources and energy per unit GDP in our country is two to three times higher than in the countries of Western Europe, the USA and Japan.

On the other hand the producers of ceramic wall materials complain that the reserves of clay not requiring serious and often expensive modification are exhausted [2].

These problems can be solved effectively by increasing the use of industrial wastes. Raw materials from wastes are two to four times cheaper than natural materials, fuel consumption in the production of construction materials decreases by 10 – 40% and the specific capital investments decrease by 30 – 50%.

Using modern methods of research scientists at VNIISTROM have studied the structural particulars of clays from several deposits and commercial wastes from a number of petrochemical plants in the Republic of Tatarstan.

A Bruker D2 Phaser diffractometer was used to investigate the mineral composition of clays. A quantitative analysis was performed in the Difrac.eva program using the peak values of the interplanar reflections neglecting the amorphous component of the sample (Table 1).

A HORIBA LA-950 particle size distribution analyzer was used to perform a granulometric analysis and determine the change produced in the granulometric composition by ultrasonic action.

The average particle size of clays from the Khlystovskoe deposit is 34.5 μm without ultrasonic action (Fig. 1).

The average particle size was 13.6 μm after 3-min treatment (Fig. 2).

We note that after ultrasonic treatment the mass fraction of particles smaller than 10 μm increased from 5 to 35%,

TABLE 1. Mineral Composition of the Experimental Clays

Minerals	Mineral content in clays from deposits, wt.%			
	Khlystovskoe	Sakharovskoe	Buinskoe	Salmanovskoe
Quartz	46	47	33	38
Microcline	15	10	23	–
Albite	8	12	18	39
Muscovite	13	13	21	9
Clinochlore	–	7	4	6
Montmorillonite	1	1	1	1
Calcite	6	2	–	7
Dolomite	–	4	–	–
Amphibole, hastingsite	3	3	–	–
Other aluminum silicates	8	–	–	–

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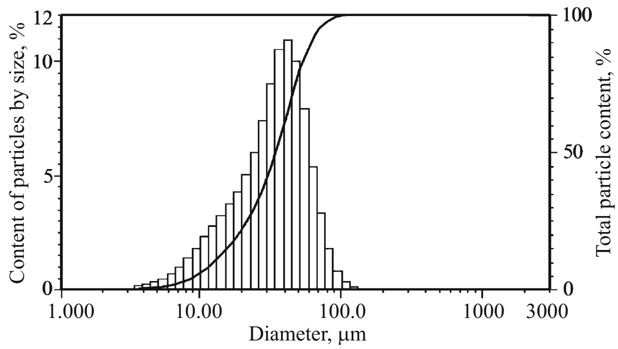

Fig. 1. Particle size distribution of clay from the Khlystovskoe deposit (without ultrasonic treatment).

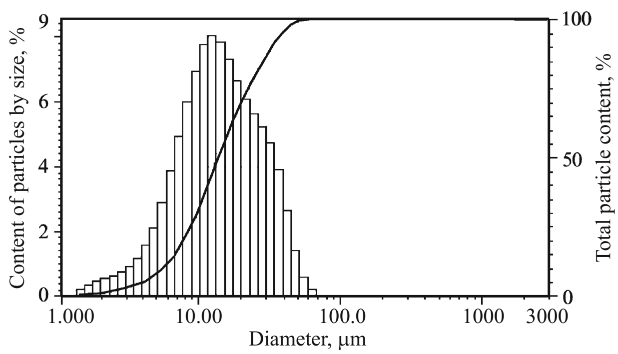

Fig. 2. Particle size distribution of clay from the Khlystovskoe deposit after ultrasonic treatment for 3 min.

while the average particle size decreased more than two-fold. Viewing ultrasonic treatment as a form of mechanical activation of raw material we introduced the appropriate recommendations into the technological regulations for the preparation of clay.

Using an XRD-7000S diffractometer (Shimadzu, Japan) with a high-temperature attachment we traced the change in the mineral composition with increasing temperature. The mineral composition was studied every 100°C, which requires 30 min in each case. Next, the temperature was raised once again by 100°C and the composition was investigated.

It found that in the course of firing the mineral composition of the initial composition changes considerably depending on its mineral composition and temperature. For example, in a raw composition with high carbonate content (clays from the Salmanovskoe deposit) the crystalline embryos in the form of calcium silicates already form at 800°C.

We investigated the change in the mineral composition in the temperature interval 1050 – 1150°C in greater detail (Table 2).

The elemental composition according to the x-ray spectrum of a macroscopic section of clay from the Khlystovskoe deposit is as follows (%): 2.3 C, 67.7 O, 0.6 Na, 1.1 Mg, 5.6 Al, 18.9 Si, 0.9 K, 0.8 Ca, 0.2 Ti, and 2.0 Fe. The iron in clay is represented either in the form of amorphous hydroxide $Fe(OH)_2$ or in a composition of complex aluminum hydrosilicates containing magnesium and iron together with silicon and aluminum. Hematite increases with increasing firing temperature and correspondingly the article acquires a darker color.

As a result of firing at 1150°C ceramic samples made from Khlystovskoe clay, just as clays from other deposits, have low water absorption (2 – 3%), but the cracks appearing during firing do not permit reaching high strength. This requires the use of additives to modify clays. We used wastes from petrochemical enterprises in the Republic of Tatarstan for such modifiers.

One example of industrial wastes, referred to below as modifier *X*, is the highly disperse waste from the glass-fiber plant at Tatneft' JSC. This waste is comprised of 90% amorphous silica with an admixture of alkali elements. It also contains extremely fine glass fibers. In its pure form the modifier *X* after formation under pressure and firing at 700°C forms a dense structure with 1.5% water absorption. The characteristics of modifier *X* manifest when it is used in a composition with amorphous silica. This raw material mixture in a 2 : 1 ratio acquires high strength (103 MPa) at firing temperature 800°C; the water absorption is only 1.8%. Investigations in an electron microscope revealed a very nonuniform structure (Fig. 3).

The mineral composition of the sample obtained is as follows (mass fraction, %): quartz 18, cristobalite 56 and microcline 26. It was proposed on the basis of the results obtained that modifier *X* be used as an additive in Khlystovskoe clay.

The raw compositions with the modifier *X* are very sensitive to the firing temperature and the percentage content of the modifier (Table 3).

A characteristic break in an intergrain boundary is shown in Fig. 4. Analysis of the photographs suggests that the grains are densely packed and the intergrain boundary serves as a kind of glue. Under a load the material fractures along grain boundaries.

TABLE 2. Change in the Phase Composition of Khlystovskoe Clay during Firing

Mineral	Mineral content (wt.%) after firing at temperature, °C			
	before firing	1050	1100	1150
Quartz	46	64	52	44
Microcline	15	14	22	14
Albite	8	20	24	39
Hastingsite	3	–	–	–
Muscovite	13	–	–	–
Montmorillonite	1	–	–	–
Calcite	6	–	–	–
Other aluminum silicates	8	–	–	–
Hematite	–	2	2	3

TABLE 3. Characteristics of Khlystovskoe Clay Samples with Modifier *X*

Index	Firing temperature, °C	Properties of fired samples* with modifier *X* content, wt.%				
		2	4	6	8	16
Density, g/cm^3	1030	1.85	1.87	1.91	1.95	2.15
	1080	1.97	2.14	2.28	2.29	–
Water absorption, %	1030	13.5	13.2	9.2	7.3	2.4
	1080	7.8	4.5	1.8	1.8	–
Strength under compression, MPa	1080	72.5	94.2	103.8	116.2	–
Fire shrinkage, %	1080	1.8	2.8	3.8	4.9	

* Samples formed under compression (40 MPa) with diameter 50 mm and height 50 mm.

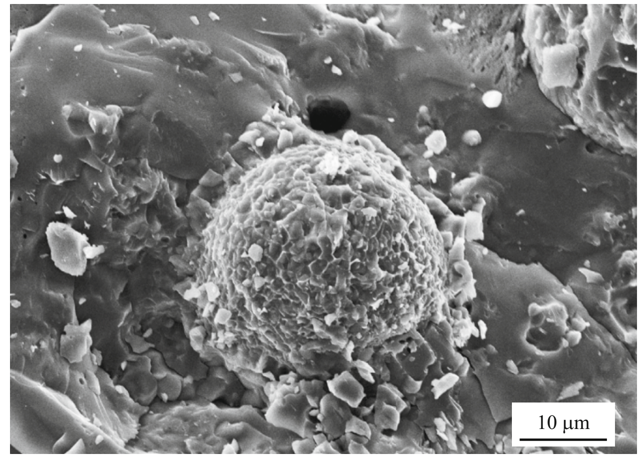

Fig. 3. SEM image of a sample of the raw material mixture comprised of modifier *X* with amorphous silicon; firing temperature 800°C.

Crack growth with subsequent fracture proceeds parallel to the axis of loading. This is characteristic for strong ceramic materials [3].

We believe that the presence in the modifier *X* of thin fibers less than 2 μm thick, which act as a kind of reinforcement material, plays a large role in the strengthening of the ceramic material (Fig. 5). Characteristically, the fibers are not melted at firing temperature 1080°C.

The fibers melt at 1150°C.

The energy dispersion spectrum of a macroscopic fragment of a sample is as follows, %: 62.8 O, 1.3 Na, 1.3 Mg, 5.5 Al, 24.0 Si, 1.4 K, 2.0 Ca, 0.1 Ti, and 1.5 Fe.

The high strength of the sample combined with low fire shrinkage is a good prerequisite for the production of facing ceramic.

The modifier *X* affects the characteristics of fired materials not only with Khlystovskoe clays but also with other clays. The character of the effect largely depends on their mineral composition. In the case of Sakharovskoe clays the samples retain adequate water absorption, but the strength is much lower than that of Khlystovskoe clays (Table 4).

Similarly modified clays from the Buinskoe deposit give firing shrinkage above 7% under identical firing conditions. This results in crack formation.

A distinguishing feature of Salmanovskoe clays is high dispersity of carbonates, which during firing form a structure

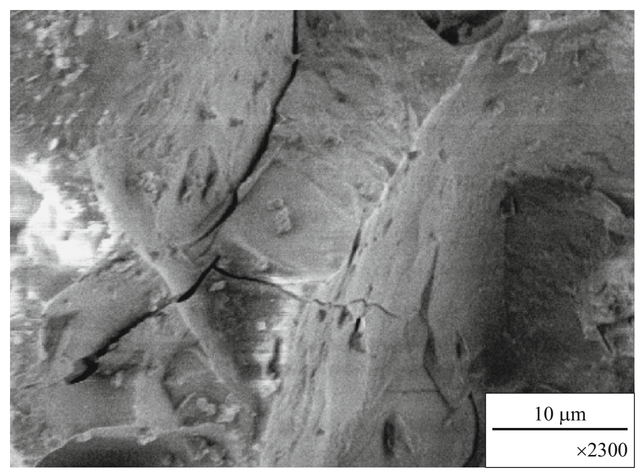

Fig. 4. SEM image of a sample comprised of Khlystovskoe clay with 5% modifier *X*; firing temperature 1080°C.

TABLE 4. Characteristics of Sakharovskoe Clay Samples with Modifier *X* with Firing Temperature 1050°C.

Index	Properties of samples with modifier *X* content, wt.%			
	5	6	7	8
Density, g/cm^3	1.76	1.83	1.89	1.97
Water absorption, %	15.5	14.0	9.8	9.2
Strength in compression, MPa	20.4	44.2	46.0	72.5

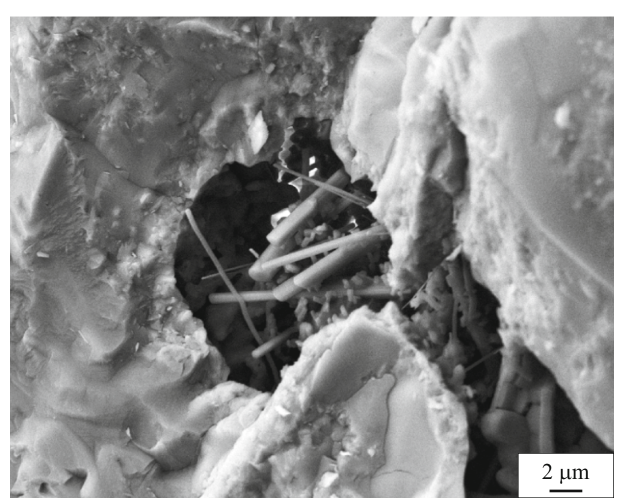

Fig. 5. SEM image of a Khlystovskoe clay sample with 5% modifier *X*; firing temperature 1080°C.

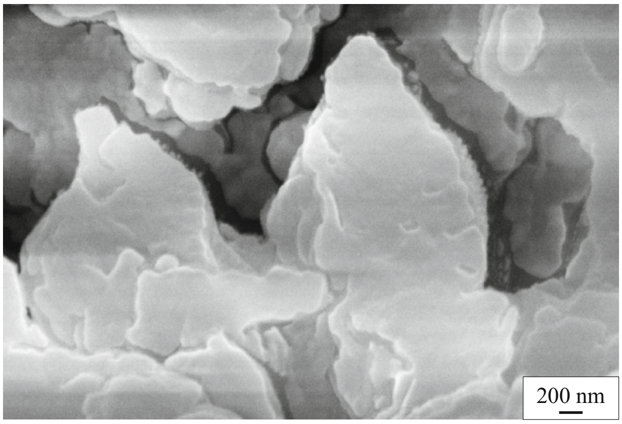

Fig. 6. SEM image of a ceramic sample made from Salmanovskoe clay.

TABLE 5. Characteristics of Fired Samples made from Khlystovskoe clays using Modifier *S*

Index	Modifier *S* content, wt.%	Properties of samples fired at temperature, °C		
		950	1000	1050
Density, g/cm^3	3	1.85	1.86	1.95
	5	1.81	1.85	1.97
Water absorption, %	3	12.4	12.2	7.5
	5	12.3	10.7	5.3
Strength in compression, MPa	3	20.2	25.5	83.8
	5	22.9	38.3	94.7

TABLE 6. Characteristics of Fired Samples Obtained from Sakharovskoe clays using Modifier *S*; Firing Temperature 1050°C

Index	Modifier *S* content, wt.%		
	2	3	5
Density, g/cm^3	1.80	1.81	1.86
Water absorption, %	11.9	9.5	7.0
Strength in compression, MPa	49.4	55.0	58.7

with nanosize pores (Fig. 6). At firing temperatures to 1100°C no fire shrinkage is observed and water absorption remains quite high (> 13%). As noted above the Salmanovskoe clays form calcium silicates even at low temperatures, so that we do not consider it efficacious to add modifier *X* to them.

We believe that modifiers containing amorphous silica with no alkali impurities will be excellent for Salmanovskoe clays.

Another industrial waste, referred to below as modifier *S*, from the same plant has a somewhat different composition and lower dispersity. Even in small quantities it makes is possible to obtain high-strength materials with low firing temperatures from clays obtained from different deposits (Table 5 and 6).

The wastes *X* and *S* totaling above 1000 tons/yr are formed only in Tatarstan, and their salvaging presents a serious problem. Similar wastes are also formed in other enterprises in the Russian Federation.

In summary, the wastes from glass fiber production make it possible not only to solve a serious environmental problem but also to increase the quality of bricks produced by manufacturers of construction ceramic articles.

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